

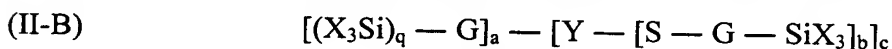
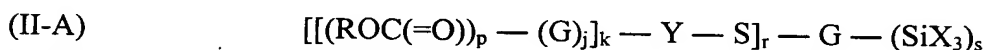
WHAT IS CLAIMED IS:

1. A process of preparing a composite of hydrophobated amorphous silica which comprises reacting said an amorphous silica having hydroxyl groups on its surface with a combination of a blocked mercaptoalkoxysilane and an alkylsilane: wherein said alkylsilane is of the general formula (I):



- wherein R is a saturated alkyl radical having from one to 18 carbon atoms, n is a value of from 1 to 3 and Z is a radical selected from a chlorine, bromine and alkoxy radicals,

wherein said blocked mercaptoalkoxysilane is selected from blocked mercaptoalkoxysilanes of the general formulas (II-A) and (II-B):



- wherein Y is a polyvalent species  $(Q_2)A(=E)$  a radical selected from the group consisting of  $-C(=NR)-$ ;  $-SC(=NR)-$ ;  $-SC(=O)-$ ;  $(-NR)C(=O)-$ ;  $(-NR)C(=S)-$ ;  $-OC(=O)-$ ;  $-OC(=S)-$ ;  $-C(=O)-$ ;  $-SC(=S)-$ ;  $-C(=S)-$ ;  $-S(=O)-$ ;  $-OS(=O)_2-$ ;  $(-NR)S(=O)_2-$ ;  $-SS(=O)-$ ;  $-OS(=O)-$ ;  $(-NR)S(=O)-$ ;  $-SS(=O)_2-$ ;  $(-S)_2P(=O)-$ ;  $-(S)P(=O)-$ ;  $-P(=S)(-)_2$ ;  $(-NR)_2P(=O)-$ ;  $(-NR)(-S)P(=O)-$ ;  $(-O)_2P(=O)-$ ;  $-(O)P(=O)-$ ;  $-(NR)P(=O)-$ ;  $(NR)_2P(=S)-$ ;  $(NR)(-S)P(=S)-$ ;  $(-O)(NR)P(=S)-$ ;  $(-O)(-S)P(=S)-$ ;  $(-O)_2P(=S)-$ ;  $-(O)P(=S)-$ ; and  $-(NR)P(=S)-$ ;

wherein the atom (A) is attached to the unsaturated heteroatom (E) which is attached to the sulfur, and the sulfur is linked via a group G to the silicon atom;

- wherein each R is independently selected from hydrogen, and straight, cyclic or branched alkyl radicals containing from 1 to 18 carbon atoms and which may or may not contain unsaturation, alkenyl groups, aryl groups, aralkyl groups containing from 1 to 18 carbon atoms;

wherein each G is independently selected from a monovalent or polyvalent

group derived from substitution of alkyl, alkenyl, aryl or aralkyl group(s) wherein G can contain from 1 to 18 carbon atoms, providing however that G is not such that said mercaptoalkoxysilane contains an alpha-, or beta- unsaturated carbonyl including a carbon-to-carbon double bond next to the thiocarbonyl group, wherein if G is univalent  
5 (e.g. if  $p=0$ ), then G can be a hydrogen atom;

wherein X is independently selected from the group consisting of  $-\text{Cl}$ ,  $-\text{GR}$ ,  $\text{RO}-$ ,  $\text{RC}(=\text{O})-$ ,  $\text{R}_2\text{C}=\text{NO}-$ ,  $\text{R}_2\text{NO}-$ , or  $\text{R}_2\text{N}-$ ,  $-\text{R}$ ,  $-(\text{OSiR}_2)$ ,  $(\text{OSiR}_3)$ , wherein each R and G is as above and at least one X is not  $-\text{R}$ ;

wherein Q is selected from oxygen, sulfur or  $(-\text{NR}-)$ ;

10 wherein A is selected from carbon, sulfur, phosphorous or sulfonyl;

wherein E is selected from oxygen, sulfur or  $\text{NR}$ ;

wherein p is 0 through 5; r is 1 through 3; z is 0 through 2; q is 0 through 6; a is 0 through 7; b is 1 through 3; j is 0 to 1, but j is 0 only if p is 1 and c is from 1 through 6, wherein j is preferably from 1 through 4; t is 0 through 5; s is 1 through 3; k is 1 or 2;

15 and

wherein,

(A) if A is carbon, sulfur or sulfonyl, then

(1)  $a+b=2$  and

(2)  $k=1$ ;

20 (B) if A is phosphorus and  $a+b=c$  unless both

(1)  $c>1$  and

(2)  $b=1$ , in which case  $a=c+1$ , and

(C) if A is phosphorus, then k is 2.

25 2. The process of claim 1 wherein alcohol and hydrogen halide byproducts formed by chemical reaction of said hydroxyl groups on said amorphous silica with alkoxy groups of said blocked mercaptoalkoxysilane and with alkoxy and/or halogen groups of said alkylsilane are removed from said hydrophobated amorphous silica composite.

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3. A composite prepared according to the process of claim 1.

4. A composite prepared according to the process of claim 2.

5. A method of preparing a rubber composition comprises:

(A) mixing at least one conjugated diene-based elastomer with said hydrophobated amorphous silica composite of claim 4;

(B) mixing an unblocking agent with the resulting mixture of step (A), and

5 (C) sulfur vulcanizing the resulting mixture.

wherein chemical activity of the blocked mercapto group of said hydrophobated amorphous silica is substantially blocked insofar as interaction with said diene-based elastomer is concerned, and

10 wherein said blocked mercapto group of said hydrophobated amorphous silica is unblocked by said unblocking agent, and

wherein said unblocked mercapto group interacts with at least one of said diene-based elastomers to couple said hydrophobated amorphous silica to at least one of said elastomers.

15 6. The method of claim 5 wherein said blocked mercaptoalkoxysilane is the blocked mercaptoalkoxysilane of Formula (II-A).

20 7. The method of claim 5 wherein said blocked mercaptoalkoxysilane is the blocked mercaptoalkoxysilane of Formula (II-A) wherein  $r=1$  and  $s=1$ ; Y is  $\text{—C(=O)—}$ ; and X is  $\text{RO—}$ .

8. The method of claim 5 wherein said unblocking agent is selected from at least one of N,N'-diphenylguanidine and N,N'-di-ortho-tolylguanidine.

25 9. The method of claim 5 which comprises, based on parts by weight per 100 parts by weight (phr) of diene-based elastomer:

(A) mixing at least one conjugated diene-based elastomer with about 10 to about 120 phr of reinforcing filler at a temperature in a range of from about 140°C to about 170°C, wherein said reinforcing filler is comprised of

30 (1) said hydrophobated amorphous silica composite of claim 4, and optionally,

(2) at least one additional reinforcing filler selected from carbon

black and an additional synthetic amorphous silica, and optionally, a coupling agent for said additional synthetic amorphous silica,

(B) mixing an unblocking agent with the mixture of step (A), at a temperature in a range of from about 100°C to about 125°C and concurrently or thereafter mixing sulfur curative therewith at a temperature in a range of from about 100°C to about 125°C, and thereafter,

(C) curing the resulting mixture at an elevated temperature in range of from 140°C to about 170°C.

10            10. The method of claim 5 wherein said alkylsilane is selected from the group consisting of trichloro methyl silane, dichloro dimethyl silane, chloro trimethyl silane, trimethoxy methyl silane, dimethoxy dimethyl silane, methoxy trimethyl silane, trimethoxy propyl silane, trimethoxy octyl silane, trimethoxy hexadecyl silane, dimethoxy dipropyl silane, triethoxy methyl silane, triethoxy propyl silane, triethoxy octyl silane, and diethoxy dimethyl silane.

11. The method of claim 5 wherein for blocked mercaptoalkoxysilanes: Y is  $\text{RC(=O)—}$ ,  $p = 0$ ,  $r = 1$ ,  $s = 1$ , X is  $(\text{RO—})$ , R is an alkyl group having from 1 to 18 carbon atoms, and G is a monovalent alkyl radical having from 1 to 18 carbon atoms.

12. The method of claim 5 wherein said blocked mercaptoalkoxysilanes are selected from at least one of the group consisting of 2-triethoxysilyl-1-ethyl thioacetate; 2-trimethoxysilyl-1-ethyl thioacetate; 2-(methyldimethoxysilyl)-1-ethyl thioacetate; 3-trimethoxysilyl-1-propyl thioacetate; triethoxysilylmethyl thioacetate; trimethoxysilylmethyl thioacetate; triisopropoxysilylmethyl thioacetate; methyldiethoxysilylmethyl thioacetate; methyldimethoxysilylmethyl thioacetate; methyldiisopropoxysilylmethyl thioacetate; dimethylethoxysilylmethyl thioacetate; dimethylmethoxysilylmethyl thioacetate; dimethylisopropoxysilylmethyl thioacetate; 2-triisopropoxysilyl-1-ethyl thioacetate; 2-(methyldiethoxysilyl)-1-ethyl thioacetate; 2-(methyldiisopropoxysilyl)-1-ethyl thioacetate; 2-(dimethylethoxysilyl)-1-ethyl thioacetate; 2-(dimethylmethoxysilyl)-1-ethyl thioacetate; 2-(dimethylisopropoxysilyl)-1-ethyl thioacetate; 3-triethoxysilyl-1-propyl thioacetate; 3-triisopropoxysilyl-1-propyl thioacetate; 3-methyldiethoxysilyl-1-propyl thioacetate;

- 3-methyldimethoxysilyl-1-propyl thioacetate; 3-methyldiisopropoxysilyl-1-propyl thioacetate; 1-(2-triethoxysilyl-1-ethyl)-4-thioacetylcyclohexane;  
1-(2-triethoxysilyl-1-ethyl)-3-thioacetylcyclohexane;  
2-triethoxysilyl-5-thioacetylnorbornene; 2-triethoxysilyl-4-thioacetylnorbornene;  
5 2-(2-triethoxysilyl-1-ethyl)-5-thioacetylnorbornene;  
2-(2-triethoxysilyl-1-ethyl)-4-thioacetylnorbornene;  
1-(1-oxo-2-thia-5-triethoxysilylpenyl)benzoic acid; 6-triethoxysilyl-1-hexyl thioacetate;  
1-triethoxysilyl-5-hexyl thioacetate; 8-triethoxysilyl-1-octyl thioacetate;  
1-triethoxysilyl-7-octyl thioacetate; 6-triethoxysilyl-1-hexyl thioacetate;  
10 1-triethoxysilyl-5-octyl thioacetate; 8-trimethoxysilyl-1-octyl thioacetate;  
1-trimethoxysilyl-7-octyl thioacetate; 10-triethoxysilyl-1-decyl thioacetate;  
1-triethoxysilyl-9-decyl thioacetate; 1-triethoxysilyl-2-butyl thioacetate;  
1-triethoxysilyl-3-butyl thioacetate; 1-triethoxysilyl-3-methyl-2-butyl thioacetate;  
1-triethoxysilyl-3-methyl-3-butyl thioacetate; 3-trimethoxysilyl-1-propyl thiooctoate;  
15 3-triethoxysilyl-1-propyl thiopalmitate; 3-triethoxysilyl-1-propyl thiooctoate;  
3-triethoxysilyl-1-propyl thiobenzoate; 3-triethoxysilyl-1-propyl thio-2-ethylhexanoate;  
3-methyldiacetoxysilyl-1-propyl thioacetate; 3-triacetoxysilyl-1-propyl thioacetate;  
2-methyldiacetoxysilyl-1-ethyl thioacetate; 2-triacetoxysilyl-1-ethyl thioacetate;  
1-methyldiacetoxysilyl-1-ethyl thioacetate; 1-triacetoxysilyl-1-ethyl thioacetate;  
20 3-ethoxydidodecyloxy-1-propyl thioacetate; 3-ethoxyditetradecyloxy-1-propyl thioacetate;  
3-ethoxyditetradecyloxy-1-propyl-thiooctoate;  
3-ethoxydidodecyloxy-1-propyl-thiooctoate; 3-ethoxyditetradecyloxy-1-propyl thioacetate;  
3-ethoxydidodecyloxy-1-propyl-thiooctate;  
3-ethoxyditetradecyloxy-1-propyl-thiooctoate;  
25 tris-(3-triethoxysilyl-1-propyl)trithiophosphate;  
bis-(3-triethoxysilyl-1-propyl)methyldithiophosphonate;  
bis-(3-triethoxysilyl-1-propyl)ethyldithiophosphonate;  
3-triethoxysilyl-1-propyldimethylthiophosphinate;  
3-triethoxysilyl-1-propyldiethylthiophosphinate;  
30 tris-(3-triethoxysilyl-1-propyl)tetrathiophosphate;  
bis-(3-triethoxysilyl-1-propyl)methyltrithiophosphonate;  
bis-(3-triethoxysilyl-1-propyl)ethyltrithiophosphonate;  
3-triethoxysilyl-1-propyldimethyldithiophosphinate;

- 3-triethoxysilyl-1-propyldiethyldithiophosphate;  
tris-(3-methyldimethoxysilyl-1-propyl)trithiophosphate;  
bis-(3-methyldimethoxysilyl-1-propyl)methyldithiophosphate;  
bis-(3-methyldimethoxysilyl-1-propyl)ethyldithiophosphate;  
5 3-methyldimethoxysilyl-1-propyldimethylthiophosphate;  
3-methyldimethoxysilyl-1-propyldiethylthiophosphate;  
3-triethoxysilyl-1-propylmethylthiosulphate;  
3-triethoxysilyl-1-propylmethanethiosulphonate;  
3-triethoxysilyl-1-propylethanethiosulphonate;  
10 3-triethoxysilyl-1-propylbenzenethiosulphonate;  
3-triethoxysilyl-1-propyltoluenethiosulphonate;  
3-triethoxysilyl-1-propylnaphthalenethiosulphonate;  
3-triethoxysilyl-1-propylxylenethiosulphonate; triethoxysilylmethylmethylthiosulphate;  
triethoxysilylmethylmethanethiosulphonate; triethoxysilylmethylethanethiosulphonate;  
15 triethoxysilylmethylbenzenethiosulphonate; triethoxysilylmethyltoluenethiosulphonate;  
triethoxysilylmethylnaphthalenethiosulphonate and  
triethoxysilylmethylxylenethiosulphonate.

13. The method of claim 5 wherein the unblocking agent is a nucleophile  
20 containing a hydrogen atom sufficiently labile such that hydrogen atom can be  
transferred to the site of the original blocking group to form the mercaptoalkoxysilane.

14. The method of claim 5 wherein said unblocking agent is a nucleophile  
selected from the group consisting of amines, imines and guanidines that contain at  
25 least one N-H bond.

15. The method of claim 5 wherein said rubber composition is free of  
functionalized siloxanes.

16. A rubber composition prepared by the method of claim 5.  
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17. The rubber composition of claim 16 wherein said diene-based elastomer  
is comprised of at least one of homopolymers and copolymers of at least one of

isoprene and 1,3-butadiene, copolymers of styrene and/or alphas-methylstyrene with at least one of isoprene and 1,3-butadiene, tin coupled organic solution polymerization prepared styrene/butadiene copolymers and amine and silane functionalized organic solution polymerization prepared styrene/butadiene copolymers and cis

5 1,4-polybutadiene elastomers.

18. An article of manufacture having at least one component comprised of the rubber composition of claim 16.

10 19. A tire having at least one component comprised of the rubber composition of claim 16.

20. A tire having at least one component comprised of the rubber composition of claim 17.